

Fundamental Mechanisms in High-Carbon Fly Ash Utilization

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OBJECTIVE

The objective of this project is to understand the basic mechanisms leading to problems in the utilization of high-carbon ash from pulverized solid fuel combustion. Low NO_x retrofits have led to significant increases in ash carbon content at many utility sites, and this has led to widespread problems with the economic and environmental utilization of fly ash, especially in the commercially important concrete market, where ash is used as a partial replacement for Portland cement [Hurt and Gibbons, 1995, Hill et al., 1997]. Ash use in concrete is beneficial for a number of reasons: it increases long term strength, decreases permeability, reduces cement costs, reduces the rate of heat release from hydration reactions, and represents a net decrease in CO_2 emissions. The CO_2 benefit is achieved by avoiding CO_2 emissions associated with cement manufacture both through fuel use and limestone calcination. In this sense, fly ash utilization in concrete and the corresponding avoidance of cement production represents a form of mineral sequestration of carbon.

PROGRESS TO DATE

Work to date has focused on ash utilization in various concrete applications. In most concrete varieties, carbon in ash acts as an adsorbent that interferes with the action of specialty surfactants, so-called air entraining admixtures (AEAs) that stabilize submillimeter air bubbles in the paste. For this project, a suite of 56 ash samples has been assembled, representing a variety of geographic regions in the U.S, parent coals, unit types and firing configurations, and inorganic ash chemistries. Most of the samples were typical of ordinary operation, though a few were known to be of unusual character, having been deliberately prepared under “upset” conditions. Some of the samples were prepared by using electrostatic separation techniques (Separation Technology, Inc.) The fly ashes could be categorized using the usual ASTM classification system into three main types: class C, class F and petroleum coke co-fired fly ashes. We have characterized the adsorptive behavior toward concrete AEAs for each of these samples, and have measured a number of other properties to understand the source of the variations in adsorptivity. This work is described in detail below.

Experimental

Loss-On-Ignition measurements

Loss-on-ignition (LOI) tests were performed on 1 gram samples, which were placed into small pre-weighed porcelain crucibles and then pre-dried in a laboratory oven at 130°C for two hours. After drying, samples were placed into a desiccator for cooling down to room temperature and then re-weighed. The samples were then placed into an air ventilated laboratory oven at 740°C for two hours, after which the samples were again cooled down in a desiccator and re-weighed. This is basically the standard ASTM procedure, and it was verified that the two-hour combustion achieved

constant weight. The change in weight between heating at 130°C and 740°C was the reported LOI, and is assumed to be the weight of unburned carbon in the original sample. Each fly ash sample was analyzed at least twice and an average percentage weight loss was calculated. The typical variance in the LOI values was quite small, and only in some cases did it get as high as 5% (relative basis), especially in ashes with LOI values lower than 0.5%.

Foam Index test

The Foam Index test is a quick way to determine the suitability of a particular fly ash as a concrete additive. In our work, we examined two commonly used AEAs: Darex IITM from Grace Construction Products and Air 40TM from Boral Material Technologies, Inc. The Foam Index tests involved placing two grams of fly ash, 8 grams of Portland cement and 25 ml of deionized water into a 70 ml cylindrical jar with a 40 mm-I.D. and 80 mm length. The jar was capped and thoroughly shaken for one minute to completely wet the cement and ash. A 10 vol.-% aqueous solution of AEA was then added one drop (0.02 ml) at a time from a pipette gun. After addition of each drop the jar was capped and shaken for approximately 15 seconds, after which the lid was removed and liquid surface was observed. Before the endpoint of the test, the foam on the liquid surface is unstable. The endpoint was taken to occur when foam remained on the surface at least 45 seconds. A blank value was measured using only Portland cement in water. Subtraction of the blank from the actual test results gave the reported Foam Index (FI) value for the fly ash (in ml). The two different AEAs gave results that were related by a simple multiplicative factor, and results will therefore be given only for a single AEA (the Darex-II).

Gas Adsorption

In order to determine the surface area and porosity of fly ash samples, N₂ gas adsorption experiments were performed using an Autosorb-1 system from Quantachrome Corp. Low surface area samples required a slightly different procedure than the high carbon fly ash samples. To get reliable results with this apparatus, at least 10 m² of ash area was required in the sample holder. The typical surface areas for ashes with 2-5% LOI were between 2-3 m²/g, so at least 3.5g sample was required in order to get the required accuracy. For this purpose a non-standard larger capacity sample holder was used.

The fly ash sample was placed into the appropriately sized sample holder and, prior to the analysis, was outgassed for several hours at constant temperature (573 K) in vacuum. Twenty adsorption and twenty desorption points were obtained, and from these sample porosity and surface area were determined. The Brunauer, Emmet and Teller (BET) theory was used for calculating surface areas. Dubinin-Radushkevitch (DR) theory [Patrick, 1995] was used for determining the microporosity of the fly ash samples. The main source of micropores in fly ashes is carbon. The inorganic part of the ash contains mostly macro- and mesopores.

Flow Microcalorimetry

Flow microcalorimetry experiments were performed using a Mark 3V Flow Microcalorimeter (FMC) manufactured by Microscal, Ltd. of London. These experiments involved measurement of the heats of adsorption of butanol on the (polar) surface of the sample. The sample cell (0.20 ml) was filled with approximately 0.15 ml of dry sample, which was washed into place with carrier fluid (heptane). Thermistors in the sample cell provide a temperature difference related to the heat release during adsorption. Measurements were made with the sample cell just above room temperature. Perfusor VI syringe pumps were used to maintain a constant 6.5 ml/hour flow of carrier fluid in the system. The calorimeter baseline was established over several hours using the pure carrier fluid, heptane. The adsorbate, n-butanol, was dissolved in the heptane carrier and introduced from a second syringe. The method has been described in detail elsewhere [Groszek, 1987,1989], and effectively involves titration of polar surface groups by butanol. Typically the saturation endpoint is observed by the time the butanol concentration in the heptane reaches about 1% by volume. The system was calibrated by feeding a known voltage, for a controlled time, to a

precision resistor embedded in the sample cell. The polar surface area was determined using a published conversion factor, which for n-butanol on carbon is $6.7 \text{ m}^2/\text{J}$ of adsorption heat.

SELECTED RESULTS

Our earlier work [Freeman et al., 1997, Gao et al., 1997] has shown that the primary adsorption sites for surfactants exist on the fly ash carbon. Generally, the higher the LOI (unburned carbon content) then the greater the surface available for AEA adsorption. The deviations from the correlation of FI with surface area are due to factors not accounted for by surface area alone, e.g. the nature of the porosity or surface polarity.

The role of surface area

The main source of surface area in fly ash is its carbon. The surface area of the inorganic part of the ashes does not change much with the type of the fly ash and is $0.8 \text{ m}^2/\text{g} \pm 5\%$ for all fly ashes examined. In Figure 1 the surface area per gram carbon is shown as a function of LOI for different ashes. Carbon surface area was calculated using the nitrogen adsorption isotherm and the BET equation. Subtracting the surface area of the inorganic part ($0.8 \text{ m}^2/\text{g}$) from the total fly ash surface area and then dividing by LOI gives the carbon-based surface per gram carbon.

It can be seen that the typical class F fly ash has a carbon surface area in a range $30\text{-}70 \text{ m}^2/\text{g}$ -carbon. Some of the class F fly ashes shown have unusually high carbon surface areas. These fly ashes have generally been reported as unacceptable.

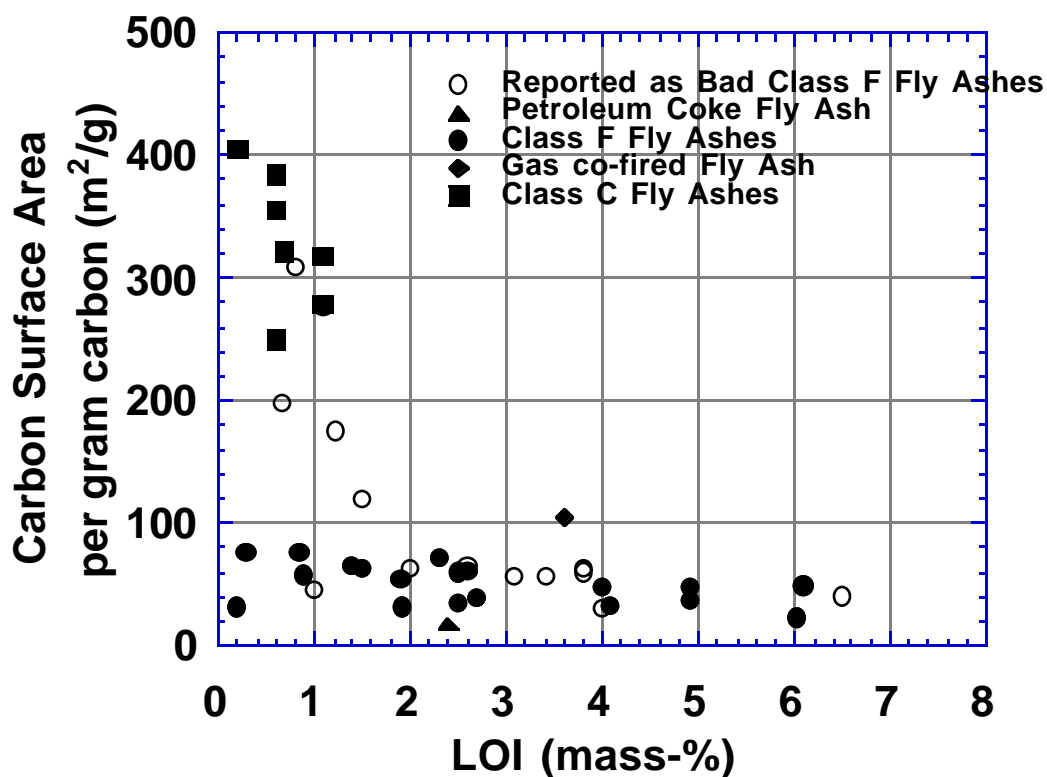


Figure 1. Surface area per gram carbon as a function of LOI for different types of fly ash.

Fly ashes from co-firing petroleum coke with coal have quite low carbon surface areas. This is because these ashes contain carbon which came mostly from the petroleum coke (96 mass-%) [Yu, 1998]. Petroleum coke is not very porous and thus its contribution to the surface area of the ash is small. As can be seen from Figure 1, all class C ashes in our sample bank have high carbon surface areas, in a range from 250-400 m²/g. It is well known that low rank coals do not soften during pyrolysis as do the bituminous coals. Instead, they cross-link into a rigid char early during pyrolysis. Thus for low rank coals, which generally give class C fly ashes, the carbon is of high surface area, containing many micropores. In bituminous coals, as the coal starts to soften, porosity is largely lost, resulting subsequently in lower carbon surface areas. It should also be noted in Figure 1 that all the class C fly ashes also have low LOI values. With low LOI, accurate calculation of surface area per gram of carbon requires that caution be exercised because of the inherent uncertainty in LOI determination. However, it is unlikely that the uncertainty in LOI measurements would bring the surface area per gram carbon down to below 200 m²/g. Thus class C fly ashes from our sample bank have higher areas per unit mass of carbon than do class F fly ashes.

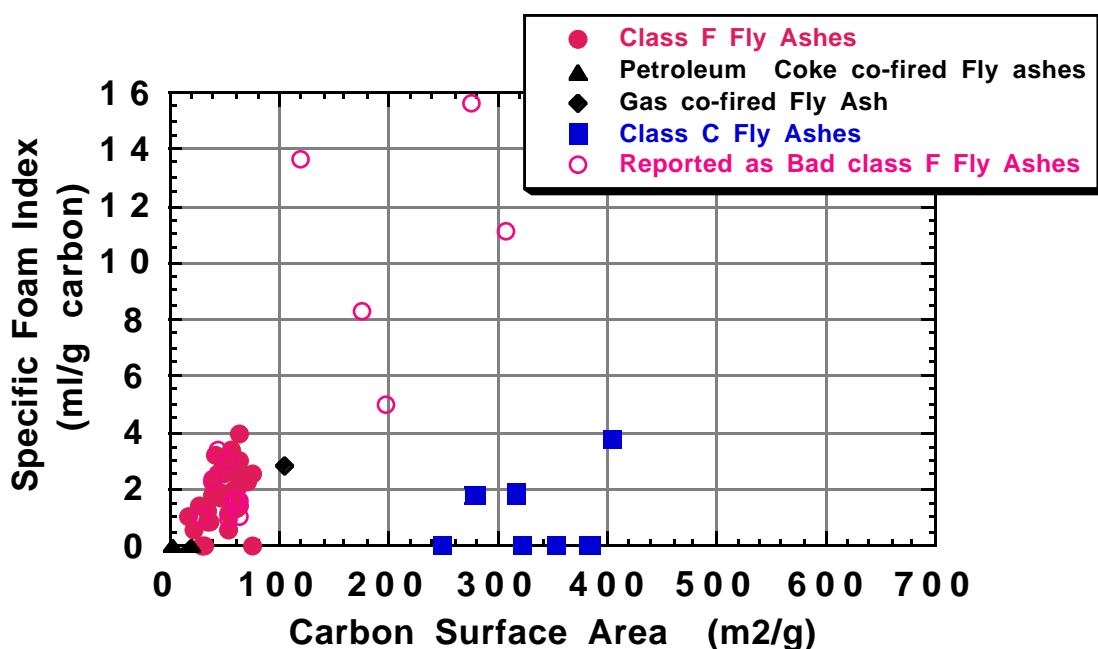


Figure 2. Specific foam index (10 vol.-% Darex II solution) per gram carbon as a function of surface area per gram carbon, for different types of fly ash.

In Figure 2, specific foam index is given as a function of surface area. Specific foam index was calculated by dividing a fly ash foam index value, in ml, by the LOI of the fly ash. Absolute values of the foam index are customarily examined to determine the quality of an ash. Here, the interest is in what carbon characteristics determine the foam index value and it is more instructive to examine a specific value. The inorganic part of the fly ash does not contribute significantly to the value of foam index.

The results of Figure 2 show that the specific foam index of a sample varies widely, even at a particular value of surface area. None of the “good” class F fly ashes had high surface area however. Thus a high foam index value seems to require high surface area, but high surface areas do not assure high specific or absolute foam index, as the class C ashes demonstrate. *Therefore*

neither LOI nor surface area alone can be used to predict acceptability of an ash. This suggests that both the accessibility of the adsorptive surface and surface polarity may also play a role.

The role of polarity

We have earlier shown that in addition to surface area, polarity is a factor that contributes to the variations in the amount of AEA uptake [Smith et al., 1997]. Polarity is determined by how many oxides (polar fractional groups) are available on the carbon surface. The inorganic part of fly ash is expected to be mostly polar, and this was verified experimentally. Thus the non-polar surface of an ash comes mostly from its non-oxidized carbon surface. Flow microcalorimetry, with n-butanol, can be used to determine this area.

Polarity can be influenced by surface oxidation. We have earlier shown that the surfaces of oxidized carbons have a lower foam index than unoxidized [Gao et al., 1997, Hachmann et al., 1998]. In this study, a sample of class F ash (FA21, 6.1% LOI) was deliberately oxidized. The specific foam index dropped from 2.49 to 0.66. Further testing showed that the porosity was not affected by the oxidation, so these results confirm that polarity plays an important role in determining foam index.

Polarity alone cannot explain all of the differences in specific foam index observed in Figure 2. For example, the class C ash surfaces are not all 100% polar. Thus another factor must also play a role. We believe this factor to be the nature of the carbon porosity.

The role of pore size distribution

Nitrogen adsorption and desorption isotherms for fly ashes and their inorganic constituents were used in the determination of the mesopore content of the fly ash carbon. The choice was made to focus in mesopores, because it was clear that the failure to correlate specific foam index with specific surface implied that micropores alone could not explain observed trends. Dubinin-Radushkevitch theory was used to determine the microporosity of the fly ash carbon. Total pore volumes were calculated at a relative pressure of 0.995. By subtracting the DR micropore volume from the calculated total pore volume and dividing that result by the LOI, the meso- plus macroporosity of the fly ash carbon (in ml/g-carbon) was determined. Due to the fact that most of this larger porosity is in mesopores, the term mesoporosity will be used for this volume. Selected fly ash samples have been picked for investigation of the influence of porosity on the specific foam index.

Figure 3 shows the fractional mesoporosity, fly ash surface area and the quality of the ash. Poorly performing ashes appear to have both a high fraction of their pore volume in mesoporosity and high surface area. This is believed to be attributable to the fact that the so-called “bad” ashes have their high surface areas made available by a network of feeder mesopores. Class C fly ashes have comparatively high surface area, but low fractional mesoporosity. Thus most of the surface area for class C fly ashes is in micropores, and these may not be accessible to the large molecular species that make up AEAs. Petroleum coke co-fired fly ash has high fractional mesoporosity, but low surface area and thus also cannot adsorb much AEA.

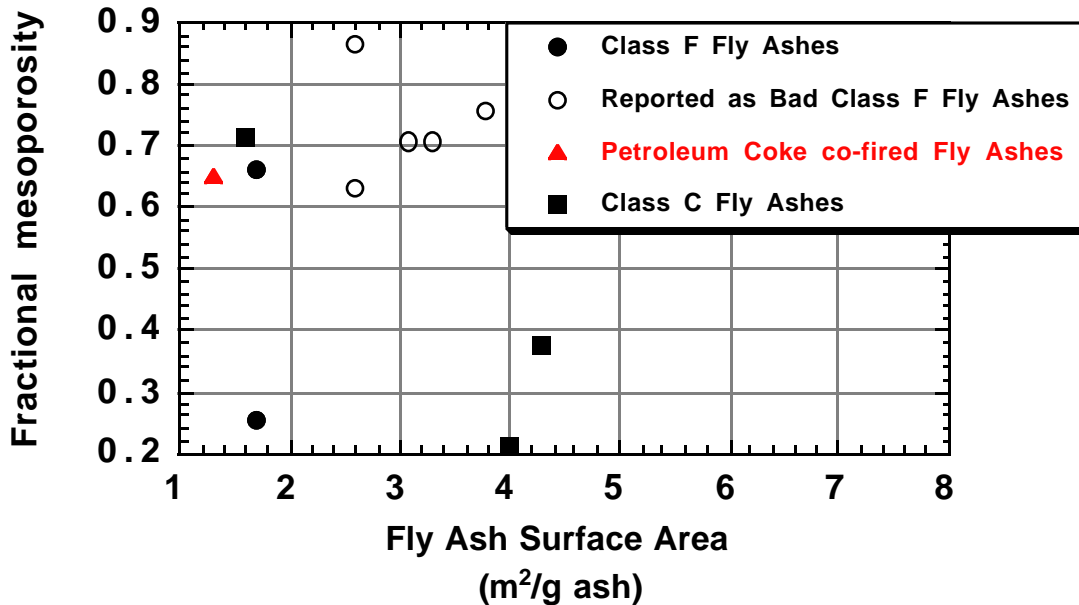


Figure 3 Fractional mesoporosity as a function of fly ash surface area.

CONCLUSIONS

1. There is no universal relationship between concrete surfactant activity and fly ash carbon content, or LOI. Generally speaking the higher the LOI of the sample, the higher the expected absolute foam index, but significant deviations occur due to the nature of the carbon present. These data establish the need for new, rational specifications for the use of carbon-containing fly ash in concrete. The suitability of a given ash for application in air entrained concrete should be assessed based on direct testing of specific adsorptivity, rather than the mass fraction of carbon (LOI).
2. Available surface area is an important factor in adsorption. Other factors being constant, a sample with higher surface area per unit mass of carbon generally gives higher adsorption of AEA. Class F fly ashes carbon have surface areas between 30-70 m²/g-carbon. Some of the class F fly ashes, reported to be problem ashes, have higher surface areas. Higher surface areas were also reported for class C fly ashes, with areas typically in the range 250-400 m²/g-carbon. However these materials had low absolute and specific foam indices. Thus factors beyond surface area must play a role in determining ash quality.
3. The nature of the carbon in fly ash explains why class C ashes having high surface areas do not have high adsorption capacities for AEA. In this case, accessibility of porosity is believed to explain the behavior. Class C fly ashes in our sample bank have carbon surface area mostly in micropores, and have few large feeder pores into the micropores. Thus large AEA molecules cannot reach the micropores.
4. The polarity of the carbon surface can also explain some differences in adsorption activities for different fly ash samples. The more oxidized the fly ash carbon, the more polar its surface, and the lower its AEA adsorption capacity.
5. Combustion modifications can potentially influence both carbon polarity and porosity, as well as total carbon content. Thus in any particular case, there are several potential reasons for changes in suitability of the fly ash for concrete utilization.

FUTURE WORK.

At some utility sites, very high carbon content ash ($> 15\%$ carbon) is produced, either from the unity directly, or as a consequence of post-combustion separation processes. Future work on the project will focus on the characterization of these high carbon ash samples as *carbon* materials, especially as potential sorbents for environmental applications. Work is underway to characterize fly ash carbons with a suite of standard adsorption tests used in the activated carbon industry, allowing direct comparison with commercial carbon products. This work will identify the most promising applications for high-carbon ash, where significant cost savings are expected over manufactured carbons. Work is also underway at Princeton University to isolate, identify, and quantify the organic extractable materials associated with coal combustion fly ash.

CONTRACT INFORMATION AND ACKNOWLEDGMENTS

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